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The research performed with support by AFOSR grant F49620-93-1-0237 for the period April 1, 1993 to June 30, 1995 is described. We developed theoretical methods and carried out calculations for multidimensional tunneling in polyatomic molecules, electronically nonadiabatic processes, unimolecular decomposition reactions, reactions in matrix-isolated molecules, and atomic diffusion in matrices; and we have made a study of the effects of introducing various constraints on the zero-point energy in classical trajectory simulations. In a collaboration with Professor Charles Wight's experimental group (University of Utah) we carried out a study of structure and vibrational spectra of the energetic molecule NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-5-one). The goal of this grant was to develop methods and to study fundamental processes of interest in many-atom systems which can potentially yield large amounts of energy upon reaction.

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**THEORETICAL CHEMICAL DYNAMICS STUDIES OF HIGH
ENERGY SPECIES**

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CONTENTS

Abstract	3
I. INTRODUCTION	4
II. RESEARCH	4
Publications	4
Brief Summaries of the Completed Research	5
Atomic Diffusion in Rare-Gas Matrices	5
Electronically Nonadiabatic Processes	6
Molecular Isomerization in Rare-Gas Matrices	7
Treating Zero-Point Energy in Classical Trajectories	8
Semiclassical Treatment of Multi-Dimensional Tunneling	9
NTO Equilibrium Structure, Force Field, and Vibrational Spectra	10
III. GRANT PERSONNEL	11

Abstract

The research performed with support by AFOSR grant F49620-93-1-0237 for the period April 1, 1993 to June 30, 1995 is described. We developed theoretical methods and carried out calculations for multidimensional tunneling in polyatomic molecules, electronically nonadiabatic processes, unimolecular decomposition reactions, reactions in matrix-isolated molecules, and atomic diffusion in matrices; and we have made a study of the effects of introducing various constraints on the zero-point energy in classical trajectory simulations. In a collaboration with Professor Charles Wight's experimental group (University of Utah) we carried out a study of structure and vibrational spectra of the energetic molecule NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-5-one). The goal of this grant was to develop methods and to study fundamental processes of interest in many-atom systems which can potentially yield large amounts of energy upon reaction.

I. INTRODUCTION

The objectives of this research program were to develop theoretical methods and perform calculations to investigate fundamental, elementary chemical dynamics processes in systems that can potentially release large amounts of energy upon reaction. The focus was on the dynamics in many-atom systems in which tunneling, electronic nonadiabatic processes, enhanced reaction due to vibrational excitation, and thermal decomposition reaction in energetic materials such as NTO. The methods developed and used are based on semiclassical mechanics, classical trajectories, and transition-state theory; some *ab initio* structural quantum mechanical computations were also used in developing potential energy surfaces.

II. RESEARCH

Further development and study of theoretical methods were a central theme of the research during the grant period. Furthermore, applications of these and existing methods were made to systems of interest in the HEDM program as well as for conventional energetic materials, namely, NTO. We describe this work in this section, but first we give a list of the publications which have resulted from the research during the grant period (1 April 1993 to 30 June 1995).

Publications

The following is a list of the publications and manuscripts (in preparation for publication) for this report period:

Dan C. Sorescu, Teresa R. L. Sutton, Donald L. Thompson, David Beardall, and Charles A. Wight, "Theoretical and Experimental Study of the Structure and Vibrational Spectra of NTO," J. Phys. Chem., submitted.

Yin Guo, Donald L. Thompson, and Thomas D. Sewell, "Analysis of the Zero-Point Energy Problem in Classical Trajectory Simulations," J. Chem. Phys., submitted.

Thomas D. Sewell, Yin Guo, and Donald L. Thompson, "Semiclassical Calculations of Tunneling Splitting in Malonaldehyde," J. Chem. Phys., in press.

Yin Guo and Donald L. Thompson, "Molecular Dynamics and Simple Transition-State Theory Predictions of Rates of Atomic Diffusion in Rare Gas Matrices," J. Chem. Phys., in press.

Paras M. Agrawal, Donald L. Thompson, and Lionel M. Raff, "Theoretical Studies of the Effects of Matrix Composition, Lattice Temperature and Isotopic Substitution on Isomerization Reactions of Matrix-Isolated HONO/Ar," J. Chem. Phys. **102**, 7000-7005 (1994).

Yin Guo, Thomas D. Sewell, and Donald L. Thompson, "A Full-Dimensional Semiclassical Calculation of Vibrational Mode Selectivity in the Tunneling Splitting in a Planar Model of Malonaldehyde," Chem. Phys. Letters **224**, 470-475 (1994).

David K. Sahm and Donald L. Thompson, "Comparison of Trajectory Surface-Hopping and Monte Carlo Phase-Space Theory Predissociation Rate Constants for N_2O ," Chem. Phys. Letters **210**, 175-179 (1993).

Brief Summaries of the Completed Research:

Atomic Diffusion in Rare-Gas Matrices

We have shown that a simple transition-state theory (STST) can be used to accurately predict classical rates of atomic diffusion in rare-gas matrices. We compared the results of STST and molecular dynamics (MD) for H-atom and C-atom diffusion in argon matrices. The results are in good agreement. The use of STST provides an considerable savings in computation time and in the amount of information about the potential needed compared with a MD or MCTST treatment. The STST calculations can be readily calculated by using only information about the system at equilibrium and the transition state. A further advantage of the STST approach is that the accuracy improves as the temperature decreases, but not the difficulty of the calculations. Molecular dynamics simulations become more expensive as the temperature decreases.

We also computed rates for H-, C- and O-atoms in xenon matrices and compared the results with the experimental results of Weitz and coworkers [J. Chem. Phys. 96, 2846 (1992) and Chem. Phys. Letters 211, 430 (1993)]. These comparisons tend to support the conclusion that there are defects present in the lattices in the experiments. While we have not done the calculations in this study, it should be possible to use STST with reasonable assumptions about lattice defects to carry out a study in which one develops a model (or models) of imperfect lattices that give agreement with the measured diffusion rates. Since we have shown that STST is valid for these processes, such a study should lead to an understanding of the nature of the lattices that leads to the various reported experimental data for atomic diffusion in rare gas matrices.

This work will soon be published: Yin Guo and Donald L. Thompson, "Molecular Dynamics and Simple Transition-State Theory Predictions of Rates of Atomic Diffusion in Rare Gas Matrices," J. Chem. Phys., in press.

Electronically Nonadiabatic Processes

We continued in this grant period research on curve crossing processes that was initiated in the previous grant period. We have carried out several calculations to study the dynamics of electronic predissociation and have suggested new theoretical methods for treating the problem. The theoretical approaches are based on the classical trajectory surface-hopping method, although we have proposed a statistical-theory method that is can be used to obtain microcanonical and canonical rates under conditions where the dynamical effects are not important. As a test case for these methods, we have studied the nonadiabatic spin-forbidden dissociation reaction $\text{N}_2\text{O}({}^1\Sigma^+) \rightarrow \text{N}_2({}^1\Sigma_g^+) + \text{O}({}^3\text{P})$.

During this grant period, we developed a Monte Carlo phase-space theory method for treating nonadiabatic unimolecular reactions in large molecules. In this

approach, the rate constant is considered to be a weighted flux through a "transition state" which corresponds to the locus of intersection of two diabatic potential-energy surfaces. Phase space points in this region contribute to the rate with weights given by the transition probabilities. The resulting expressions are evaluated by using Monte Carlo approximants. This leads to a general method that is easily applied to large systems and for general potentials. Thermal rate constants are also easily computed using this method. We have demonstrated the method for N_2O and shown that it gives results in good agreement with classical trajectory surface-hopping results.

This work has been published: David K. Sahm and Donald L. Thompson, "Comparison of Trajectory Surface-Hopping and Monte Carlo Phase-Space Theory Predissociation Rate Constants for N_2O ," *Chem. Phys. Letters* **210**, 175-179 (1993).

Molecular Isomerization in Rare-Gas Matrices

Classical dynamics calculations were carried out to study the effects of matrix composition, lattice temperature, and isotopic substitution on *cis-trans* isomerization rates and the rates of vibrational energy transfer to the lattice phonon modes for HONO, DONO, and $\text{H}^{18}\text{ON}^{18}\text{O}$ in argon matrices. The matrix-isolated isomerization rates are greater than those computed for the isolated molecules. This is attributed to a vibration→lattice motion→rotation→torsion energy transfer mechanism that enhances the isomerization rate. The isomerization process in the matrix is nonstatistical, that is, it displays vibrational mode specificity. In the gas phase (isolated molecules), D and ^{18}O substitution produce small, positive changes in the isomerization rate (13% and 26%, respectively) due to increased kinetic coupling to the torsional mode. In the matrix, however, the isotope effects are negative and of greater magnitudes. This is attributed to reduced rates of energy transfer from the lattice to rotation of the isotopic molecules which have greater moments of inertia.

This work has been published: Paras M. Agrawal, Donald L. Thompson, and Lionel M. Raff, "Theoretical Studies of the Effects of Matrix Composition, Lattice Temperature and Isotopic Substitution on Isomerization Reactions of Matrix-Isolated HONO/Ar," *J. Chem. Phys.* **102**, 7000-7005 (1994).

Treating Zero-Point Energy in Classical Trajectories

One of the potential problems with classical trajectories is aphysical flow of zero-point energy (ZPE). Quantum mechanically, within the normal mode approximation, each molecular mode is expected to contain an amount of energy at least equal to the ZPE of that mode. However, in a classical mechanical simulation of a molecule the energy can flow without this restriction among the modes yielding behavior that does not correspond to that of the real system. Recently, various methods to correct this "problem" have been suggested. Two general approaches are being used. In the "passive" methods nothing is done to alter the classical mechanics but the trajectories which violate ZPE criteria are discarded. Several "active" methods have been devised where the equations of motion are modified by the incorporation of some kind of constraint which prohibits individual trajectories from exploring regions of phase space where mode energies are less than the ZPE. The active methods can cause damage to the dynamics as we have previously shown for one of them [Sewell *et al.*, *Chem. Phys. Lett.* **193**, 512 (1992)]. In addition to this, however, is the fact that they are all based on an invalid assumption, that is, that individual trajectories should obey the ZPE criterion. In the semiclassical limit there is a one-to-one correspondence between the invariant tori in phase space and quantum mechanical eigenvalues. This correspondence is the basis of the classical trajectory method; it is assumed that an ensemble average of points on a torus corresponds to the expectation value of an observable of the quantum state. Thus, methods for correcting "the ZPE problem" that hold individual trajectories to the quantum

mechanical restrictions violate this correspondence. Quantum mechanically it is the mean value of the Hamiltonian for a given state that cannot be less than the ZPE and, correspondingly, it is the ensemble-averaged mode energies in the classical trajectories that should be expected (or required) to obey the ZPE constraints. We have used the Henon-Heiles Hamiltonian, for which quantal calculations are feasible, to illustrate the problems of several of the proposed methods for dealing with the "ZPE problem."

A manuscript been submitted to the Journal of Chemical Physics: "Analysis of the Zero-Point Energy Problem in Classical Trajectory Simulations." This work was also presented at the Conference on the Dynamics of Molecular Collisions at Asilomar, California, July, 1995.

Semiclassical Treatment of Multi-Dimensional Tunneling

Proton tunneling in polyatomic systems is sensitive to the motions of the heavy atoms. The collective motions of the heavy skeletal atoms can lead to significant variations in the height and width of the barrier through which the tunneling occurs. Thus, selective excitation of various vibrational modes of a molecule can cause large differences in tunneling rates or tunneling splittings. We have been investigating these effects and the methods for treating them [Chem. Phys. Lett. **193**, 347 (1992); J. Chem. Phys. **100**, 6445 (1994); Chem. Phys. Lett. **224**, 470 (1994)]. We are interested in treating the full dimensionalities of many-atom systems; thus we have been using semiclassical techniques in which JWKB tunneling probabilities are calculated at turning points in the "tunneling coordinate" along classical trajectories.

Tunneling splitting of the ground state of malonaldehyde serves as an excellent case for these studies because of the availability of experimental results. We have performed calculations in which all 9 atoms in malonaldehyde are allowed three-dimensional motion. The computed splittings of the pure ground state is in good

agreement with the experimental values for the parent molecule as well as for several isotopically substituted derivatives. We have also studied the effects of exciting each of the normal modes on the ground state splitting; these results show that the heavy atom motions have significant influence on the tunneling.

A manuscript been submitted to the Journal of Chemical Physics: "Semiclassical Calculations of Tunneling Splitting in Malonaldehyde." This work was also presented at the Conference on the Dynamics of Molecular Collisions at Asilomar, California, July, 1995.

NTO Equilibrium Structure, Force Field, and Vibrational Spectra

We have initiated studies of NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-5-one). Working in collaboration with Prof. Charles Wight and Mr. David Beardall, University of Utah, , we have characterized the structure and potential-energy surface near equilibrium. The experimental frequencies determined from infrared spectra of pure NTO thin films as well as for NTO molecules isolated in an argon matrix at 21 K. We computed corresponding information for the isolated molecule at the MP2/6-311G** level using the Gaussian-92 program. A force field was then developed on the basis of the theoretical and experimental results. The experimental vibrational frequencies for NTO films together with scaled fundamental frequencies from the ab initio calculations were used to construct a force field for NTO in the solid phase.

The calculated fundamental frequencies for these potentials are in good agreement with the experimental values for thin film and matrix-isolated conditions. The differences in the positions of the spectral bands indicate that environment and preparation procedure have a marked influence on the spectral characteristics of NTO.

A manuscript has been submitted to the Journal of Physical Chemistry: "Theoretical and Experimental Study of the Structure and Vibrational Spectra of NTO."

III. GRANT PERSONNEL

The personnel who worked on this project are:

Professor Donald L. Thompson, Principal Investigator

Dr. David K. Sahm, Postdoctoral Research Associate

Dr. Yin Guo, Postdoctoral Research Associate

Ms. Teresa Sutton, Graduate Assistant (Supported by an EPSCoR/ASSERT
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